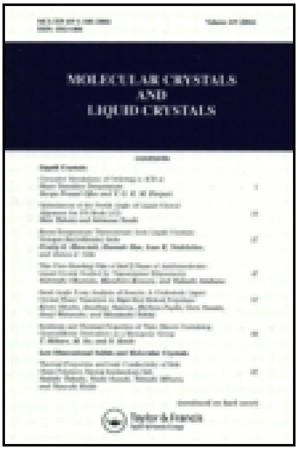

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Studies of Organic Semiconductors for 40 Years—VIII

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Studies of Organic Semiconductors for 40 Years—VIII

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Research in organic semiconductors started in China during the wake of press release of pyrolyzed polyacrylonitrile (PAN) as a semiconductor by the Academy of Sciences, U.S.S.R. in 1958. Big interest was aroused at that time in various research institutions throughout China, particularly Changchun Institute of Applied Chemistry, Institute of Physics and Institute of Chemistry, all of Academia Sinica. This wave of studies slacked up gradually and was virtually stopped in mid-sixties. Then research in this field resumed in early seventies, oriented toward the search for organic photoconductors, and materials for photovoltaic devices and electrophotography. In August 1978 Professor Martin Pope of New York University gave a series of lectures in Institute of Chemistry, Academia Sinica, Beijing, on the electronic processes in organic solids. The lecture notes supplemented with more recent developments in organic metallic conductors have been published.[1] Some fifty researchers participated in this workshop. This paved a solid road to much expanded scope of studies in organic semiconductors. For the study of organic solids interests has been diverted also to excimer and exciplex fluorescence, charge transfer complexes showing metallic conduction and superconductivity, conducting polymers since mid seventies. In the near future it is expected to widen the scope of studies on organic solids to organic ferro-magnetic compounds, Langmuir-Blodgett films and materials of non-linear optical properties.

PYROLYZED POLYACRYLONITRILE

Polyacrylonitrile (PAN) under heat treatment in air or under vacuum from 400–800°C gave products showing semiconductor properties of increasing conductivity and decreasing activation energy for conduction with increasing heat treatment temperature.[2] Structure changes during pyrolysis was followed by elemental analysis, infra-red spectra,[3,4] thermogravimetry,[5] density,[5] thermo-e.m.f.[5] and wide angle X-ray diffraction (WAXD).[6] Drastic structure changes and weight decrease were observed to occur at 400°C and above 700°. The average size of conjugation in the conjugation plane estimated from the width of WAXD peaks of (100) and (002) planes was only 1–2 nm, increasing with the heat treatment temperature from 500–1000°C. The distance between the conjugation planes showed two minima at 500 and 700°C.[6] D.C. and A.C. conductivities[7-9] and thermo-e.m.f.[10] of the

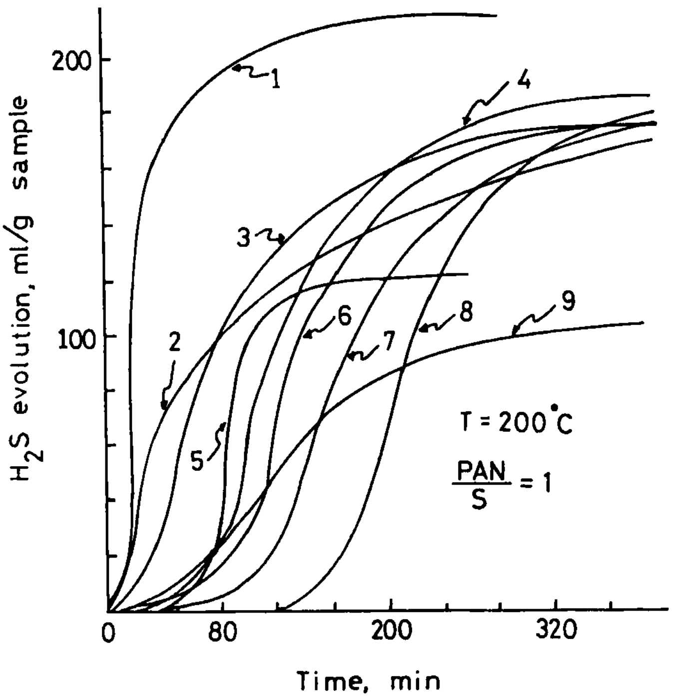


FIGURE 1 H_2S evolution at 200°C for a mixture of PAN and S(1:1) in the presence of various additives.
1—10% hydroquinone
2—no additive, preheated at 200° for 50 hr.
3—γ-ray irradiated, 10^7 Röentgen
4—10% benzoic acid
5—10% rubber vulcanization accelerator DM
6—γ-ray irradiated, 10^5 Röentgen
7—no additive
8—not deaerated before reaction
9—10% *o*-nitrobenzoic acid

pyrolyzed products were studied. Pyrolysis of PAN in the presence of $ZnCl_2$ and ZnO, Al_2O_3 and TiO_2,[11] sulfur[12] and NH_3[4] was also studied. In the presence of S the kinetics of H_2S evolution at 200°C showed an S-shaped curve with an induction period.[12] O_2 in air inhibited the reaction while the addition of 10% *p*-hydroquinone eliminated the induction period as shown in Figure 1.

By the end of sixties the interest of studies on pyrolysis of PAN was shifted to the preparation of carbon fibres. It was found that Lewis acid like $SnCl_4$ could accelerate the cyclization of PAN at 220°C without significant loss of H.[13] For $SnCl_4$ treated PAN copolymer fibre on further heat treatment a drastic conductivity increase of 7 orders of magnitude occurred at 290°C to reach a conductivity of 10^{-3} S/cm at 350°C as shown in Figure 2. In this way semiconductive fibres of a wide range of conductivities can be easily prepared. The fibre showed A.C. conductivities

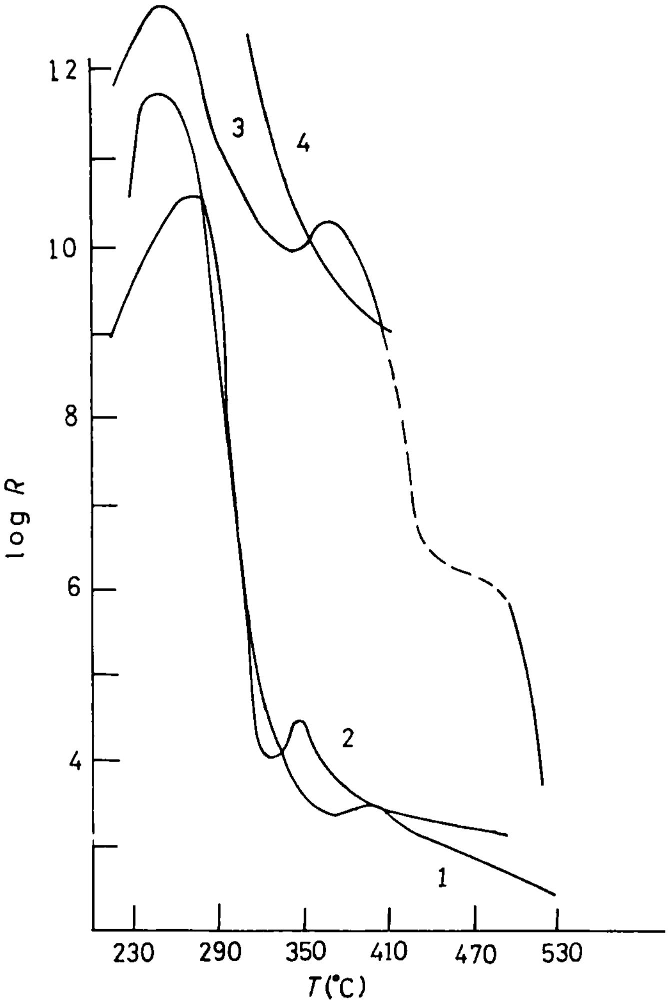
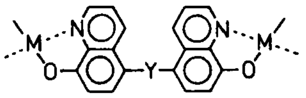


FIGURE 2 Change of resistance of PAN fiber treated with 3 wt% $SnCl_2$ in Ph_2O by thermal treatment
1—PAN copolymer I
2—PAN copolymer II
3—PAN homopolymer
4—PAN copolymer I untreated
Resistance for 10^3 fibers of total cross-area: $3.16 \cdot 10^{-2}$ cm^2, length: 1 cm.

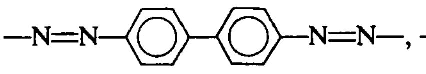
$\sigma(f) \propto f^n$ with $n = 1$ for frequencies above ca. 10^4 Hz and $n = 0.3$–0.4 for lower frequencies.[13]

SYNTHESIS OF OTHER CONJUGATED POLYMERS

Some new polymers containing extended conjugated bonds or new catalyst for such polymerization have been studied. Metal chelates of 5-bridged bis-8-hydroxyquinoline of the following structure[14]



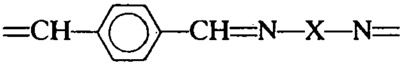
M=Cu, Ag(II), Be, Mg, Zn, Cd, Al(III), Cr(III), Mn, Fe(II), Co, Ni, Pb, VO$^+$, Pb

Y= —N=N—,  , —CH$_2$—

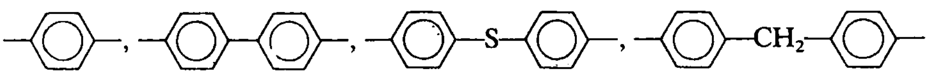
were synthesized among which transition metal complexes of Y= —N=N— showed highest conductivity reaching 10^{-7} S/cm for pressed powder compactions. However thermal stability were the lowest among them. Poly(Schiff base) of the structures

=CH—CH=N—X—N=

and



with

X= 

were synthesized.[15] The first series of the above polymers underwent cyclization reaction on heating while the second series of polymers underwent further polymerization when heated not higher than 350°C. These polymers were soluble in HCOOH. Conductivities were found to be low, 10^{-11} S/cm at 180°C.

2,3-Butanedione was polymerized in the presence of $ZnCl_2$ to a polymer at 200–400°C[21] which shows ESR signal, a conductivity of 10^{-11} S/cm and an activation energy for conduction 0.3–0.4 eV. When 2,3-butanedione was condensed with *p*-phenylenediamine an insoluble conjugated polymer of the structure $—C(CH_3)=N—C_6H_4—N=C(CH_3)—$ of similar conductivity[17] was obtained.

Phenylacetylene was polymerized with BF_3[18] and BuLi-$TiCl_4$[19] as catalyst to give polymers of molar mass 2–3 kD. Benzonitrile was polymerized in anisole with BF_3 as catalyst[20] to give polymers soluble in benzene for molar mass less than 1.2 kD and soluble in DMF for higher molar masses.

A new catalyst, π-*bis*(benzene)Cr, was found[21] for the polymerization of perfluorobutyne to the polymer $—(CF_3)C=C(CF_3)—$ with extended conjugation so that the polymer obtained is black with metallic lustre while it is still soluble in acetone. The solution showed strong absorption peaks at λ309 nm (ε 6.5 10^4) and λ273 nm (ε6.8 · 10^4). Molar mass of the polymer was determined by vapor pressure osmometry to be 1.4 kD. The polymer has a conductivity of 10^{-10} S/cm and is stable up to 150°C.

PHTHALOCYANINES (Pc)

It was observed by C_{1s} and N_{1s} XPS on PcH_2 and PcM, M being Mg, Mn, Co and Cu, that there were two C_{1s} peaks with intensity ratio of 1:3 corresponding to 8 C-atoms in the inner macro-ring and 24 C-atoms of phenyl rings. The N_{1s} XPS showed two peaks with E_b = 400.0, 398.6 eV and intensity ratio 1:3 corresponding to 2 N-atoms bonded to H and 6 equivalent N-atoms in the macro-ring. For PcM only a single N_{1s} XPS peak was observed, indicating 8 equivalent N-atoms in the macro-ring.[22] The presence of conjugated macro-ring in phthalocyanines has good evidence from XPS as well as from optical spectrum and NMR data.

PcCu is known to have numerous polymorphic forms. The characterization of various polymorphs, α-, β-, γ-, δ-, ϵ-, χ-, and π-, by WAXD, IR, VIS, DTA and density determination and the polymorphic transitions have been reviewed.[23] Density determinations in a dibromoethane (ρ_{20} = 2.18 g/cm^3)-ethanol (ρ_{20} = 0.79 g/cm^3) density gradient tube gave the following results[24]:

α-PcCu	1.641 ± 0.002	β-PcH_2	1.451 ± 0.001
β-PcCu	1.627 ± 0.001	β-PcMn	1.643 ± 0.003
χ-PcCu	1.615 ± 0.002	β-PcCo	1.636 ± 0.001
γ-PcCu	1.606 ± 0.001		

It is interesting to note that α-PcCu has the highest density of all the polymorphs while β-polymorph is the most stable one.

By a retarding field method the ionization potentials I_c for α-PcCu and β-PcCu was found to be 4.88 and 4.62 eV respectively.[25] A difference of 0.3 eV should be considered as the difference in the polarization energy of the crystalline polymorphs.

More detailed studies have been carried out on PcCu evaporated films. When PcCu was evaporated under vacuum of $5 \cdot 10^{-3}$ Pa onto Nesa glass at a film growth rate of 4.8 μm/min, the PcCu film obtained was in α-form and oriented with ($\bar{2}10$) and ($\bar{1}10$) crystalline planes (Honigmann's structure) parallel to the substrate if the substrate was not heated during evaporation.[26] Thus in the evaporated film the crystalline *b*-axis is standing up from the substrate. However, when the substrate was heated to 230–250°C the PcCu film obtained was in β-form with random orientation. When the α-PcCu evaporated film was heated above 230°C, transition to the β-form occurred but leaving the *b*-axis still standing up on the substrate. This indicates that during the polymorphic transition the PcCu stacks are not disensembled at all, only tilting of the PcCu molecular planes and changes in the interstack packing are involved in the process. Further studies showed that during the oriented growth of α-PcCu evaporated film the direction of the fastest growth, the crystalline *b*-axis, coincides with the direction of the incoming molecular beam.[27] The α-PcCu evaporated film was found to have an apparent density of 1.50 g/cm^3 as compared to the crystalline density of 1.641 g/cm^3 and a refractive index of 2.18 ± 0.13 for λ2.5–5 μm.[28]

The transition of crystalline polymorph and morphology of PcCu evaporated

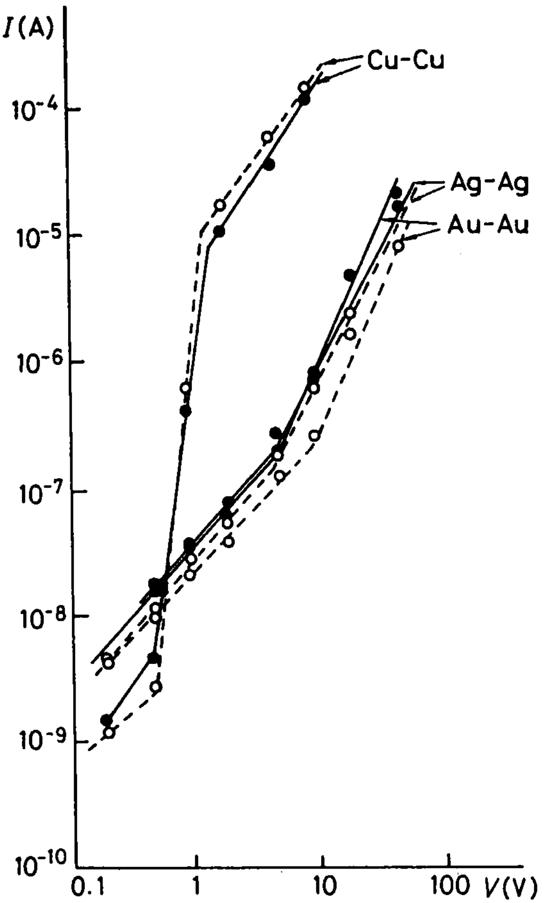


FIGURE 3 J-V curves for PcCu with Cu, Ag, Au electrodes full line: bottom electrode biased positive; broken line: bottom electrode biased negative; electrode area: 13 mm^2.

film were studied under vacuum from $8 \cdot 10^{-4}$ to $5 \cdot 10^3$ Pa during evaporation.[29] When evaporated under low vacuum, 10^3 Pa, and at high rate, 400 mg/min, X-PcCu was obtained in the form of loose cotton velvet easily blown off from the substrate by air current.[30] It can be ball-milled with $CHCl_3$ to give a fine suspension to be deposited as a film.

Volt-ampere characteristics (j-V) of α-PcCu evaporated film was studied with various combinations of electrode pairs.[31] For Cu/α-PcCu/Cu the j-V curve started from an ohmic region at low voltages and entered a space charge limited current (SCLC) region of 3.5 power dependence followed by square dependence at high applied voltages as shown in Figure 3. Only the transition from ohmic to square dependence was observed for Ag and Au electrodes. When Al was evaporated onto α-PcCu as a top electrode it showed the behavior of a blocking contact. Ag (bottom)/α-PcCu/Al (top) and Cu/α-PcCu/Al showed good rectifying effect, being conducting when Ag or Cu was biased positive. When Al was evaporated onto a

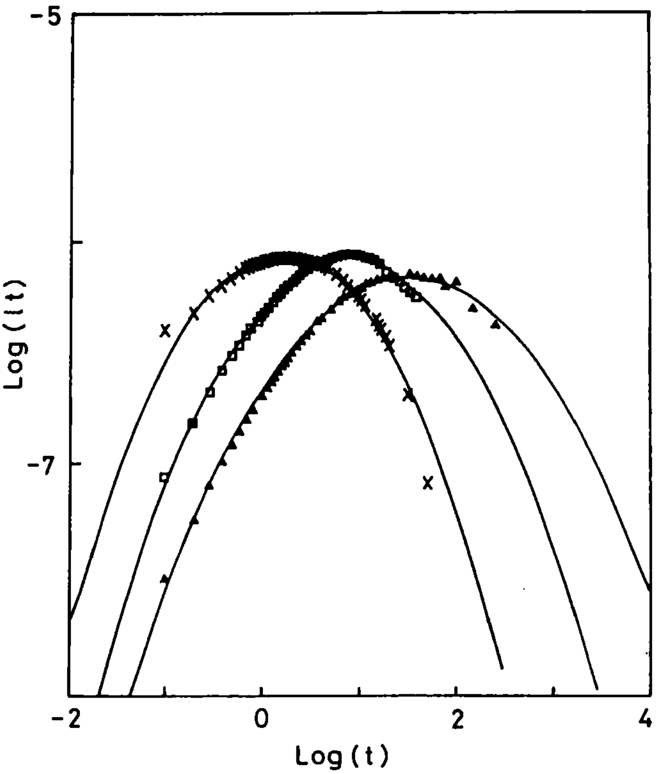


FIGURE 4 IDC spectrum of α-PcCu evaporated film at temperatures 300, 313 and 324 K. Points: observed data; curves: fitted Gaussian distribution to give trap energy level Em = 0.47 eV, width of distribution σ = 0.036 eV, total density of states N_t = 2.4 · 10^{20} cm^{-3} eV^{-1}; frequency factor ν = 1.8 · 10^7 sec^{-1}.

glass substrate as a bottom electrode and had been in contact with air before PcCu was evaporated on, it showed SCLC behavior with a Au top electrode. Al_2O_x formed on the surface of Al apparently played an important role here. SnO_2/α-PcCu/Au or Cu showed SCLC behavior in its j-V characteristics, being symmetric with respect to the polarity of applied voltages. Lot of trap states are usually present in α-PcCu evaporated film. The trap energy distribution was measured by isothermal decay current (IDC) method on a SnO_2/α-PcCu/Cu sandwich sample yielding a Gaussian distribution of trap energy at an energy level of 0.47 eV with a width of 0.036 eV and a total trap state density of 2.4 · 10^{20} cm^{-3} eV^{-1} as shown in Figure 4.[32,33]

A.C. conductivity measurements showed that the A.C. conductivity of the above type of sandwich configuration increased rather slowly from the D.C. value with increasing frequency at low frequencies and then increased as $f^{1.2}$ at frequencies above 10^5 Hz, while the electrical capacity showed a sharp decrease between 30 and 300 Hz as shown in Figure 5.[34] The photo-conduction action spectrum of α-PcCu evaporated film in sandwich configuration was almost antibatic with respect

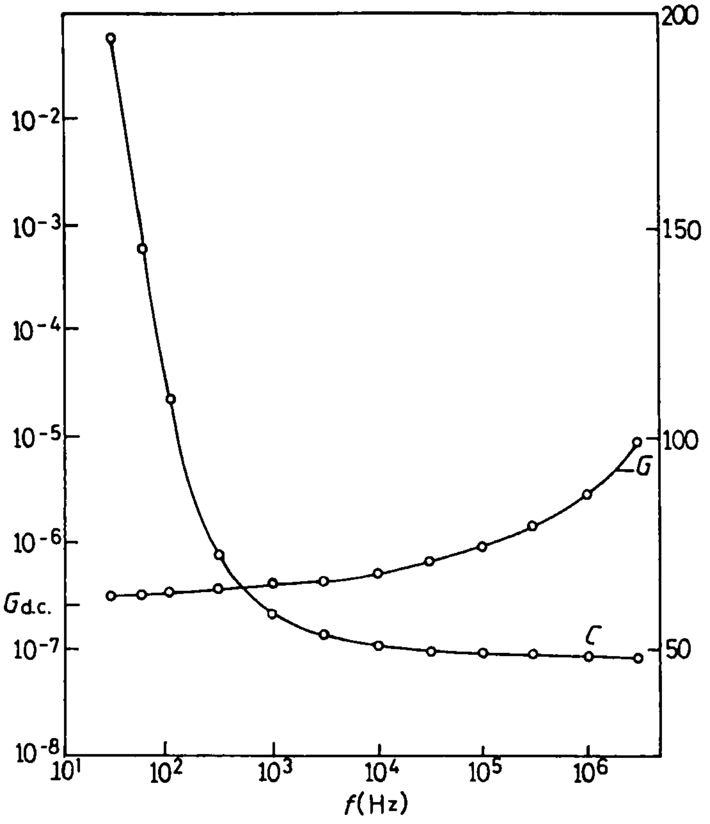


FIGURE 5 Frequency AC conductivity and capacity of α-PcCu evap. film at 17°C, Nesa glass, Cu electrodes.

to its absorption spectrum in the visible region,[35] presumably due to fast surface recombination of photogenerated carriers.

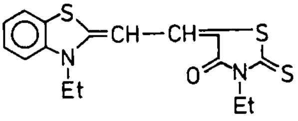
The sandwich configuration SnO_2/X-PcCu/Ag[30] showed SCLC behavior when Ag was biased negative and a ratio of photo- to dark currents of the order of 10^2 under an irradiance of 18 mW/cm^2 even at high applied fields (10^5V/cm). The activation energy for dark conduction was found to be 0.79 eV. An 18% X-PcCu dispersed in PMMA polymer matrix still possessed good photo-conductivity.

The dark conduction of a sandwich cell SnO_2/CdS, α-PcCu/Ag[36] showed the behavior of a *p*/*n* hetero-junction. It showed photo-voltaic effect to produce a V_{oc} of 0.42 V and j_{sc} of 37 μA/cm^2 under an irradiance of 7 mW/cm^2, the conversion efficiency being 0.15% (fill factor 0.3). It was found that only the photocarriers generated at the junction was effective presumably due to high recombination rate in α-PcCu evaporated film.

Pc_2Lu powder compacts showed high dark conductivity of $8 \cdot 10^{-6}$ S/cm independent of the ambient atmosphere, whether being air, vacuum or H_2.[37] The activation energy for conduction was found to be 0.21 eV.

CYANINE DYES

Many cyanine dyes including those containing a squarylium structure were synthesized and studied for its photo-conductivity and photo-voltaic effect for solar cell applications. One which has been studied more in detail is 3-ethyl-5-[2-(3-ethyl-2-benzothiazolinylidene)-ethylidene]-rhodanine (BTER) of the following structure



which contains a benzothiazole donor moiety and a rhodanine acceptor moiety in the molecule. Single crystals were grown to sufficient size to study the crystalline structure and conduction and photo-conduction properties of the crystal. When it was crystallized from pyridine solution two different crystal forms could be grown simultaneously from the same solution bath, which were proved to be polymorphs. One of them are red needles designated as α-crystal modification and the other are green platelets designated as β-crystal modification.[38] The crystalline structure parameters are listed in Table I.[39,40] The two forms differ in the molecular packing in the crystal as shown in Figure 6. The α-crystal consists of stacked columns of planar BTER molecules in diads with a molecular stacking distance of 0.357 nm within the diads and 0.372 nm between the diads. In the β-crystal diad stacking of BTER molecules still prevails with a stacking distance of 0.373 nm, but these diads are oriented with molecular planes of the neighboring diads lying almost perpendicular to each other. In both crystals the molecular packing in the diad is in such a way that the donor moiety of the molecule is stacked with the acceptor moiety of the neighboring molecule in the diad. The crystal densities found were 1.425 g/cm^3 (α-crystal) and 1.388 g/cm^3 (β-crystal).

The crystal ionization potential Ic for BTER was found to be 5.25 eV[41] by Arnold-

TABLE I

Crystal structure parameters of the α- and β-modifications of BTER crystal

α	β
Triclinic	Monoclinic
a = 0.7458 nm	a = 1.1650 nm
b = 1.0736 nm	b = 0.9026 nm
c = 1.1039 nm	c = 1.5654 nm
α = 95.16°	β = 92.24°
β = 107.16°	
γ = 103.09°	
Z = 2	Z = 4
ρ = 1.432 g cm^{-3}	ρ = 1.407 g cm^{-3}
Space group P1	$P_{21/c}$
Stacking distance	
0.357 nm in diad	0.373 nm in diad
0.372 nm between diads	

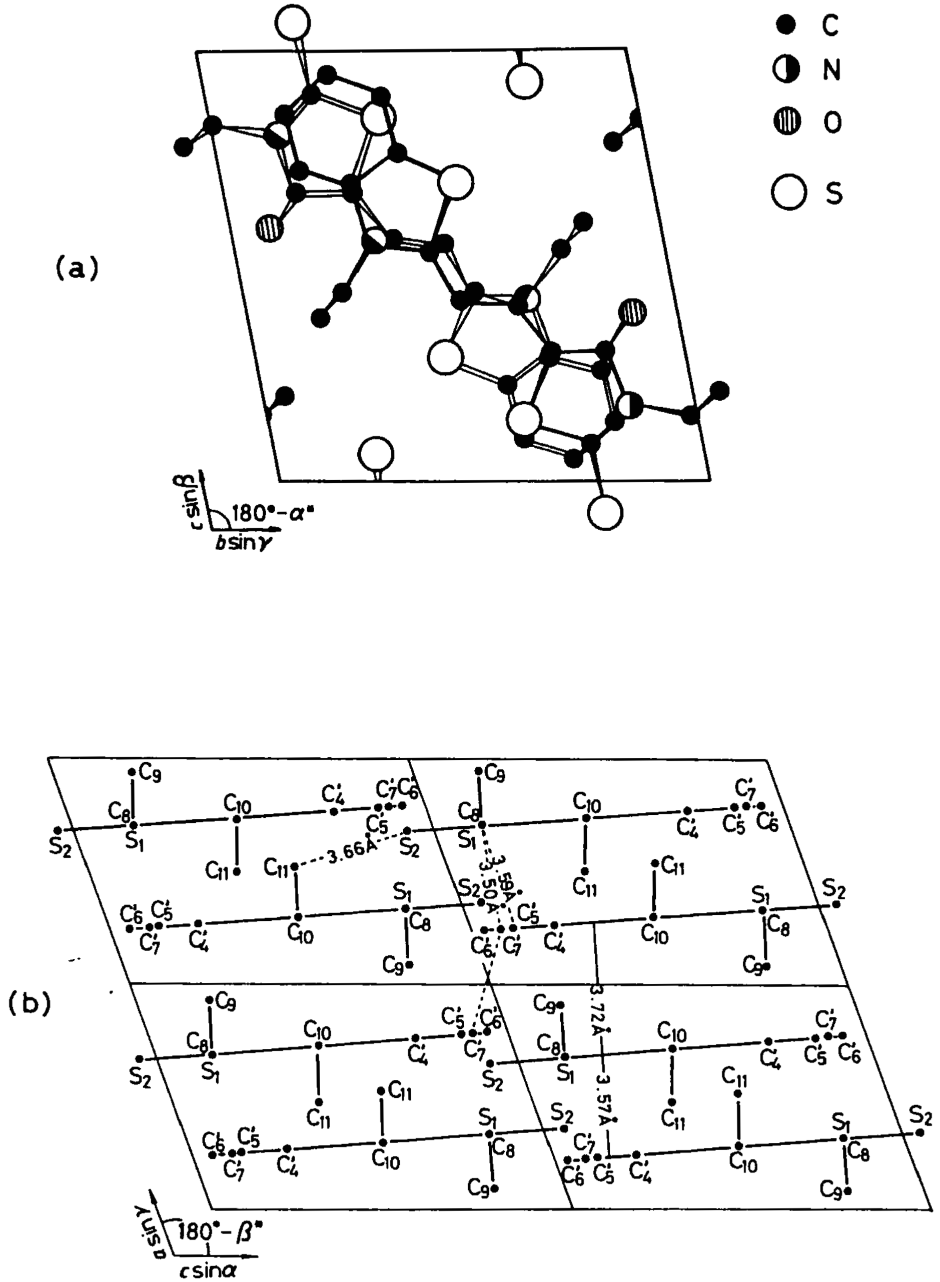


FIGURE 6 Crystal structure of α- and β-BTER: (a) α-BTER, Projection along *a*-axis; (b) α-BTER, Projection along *b*-axis; (c) β-BTER.

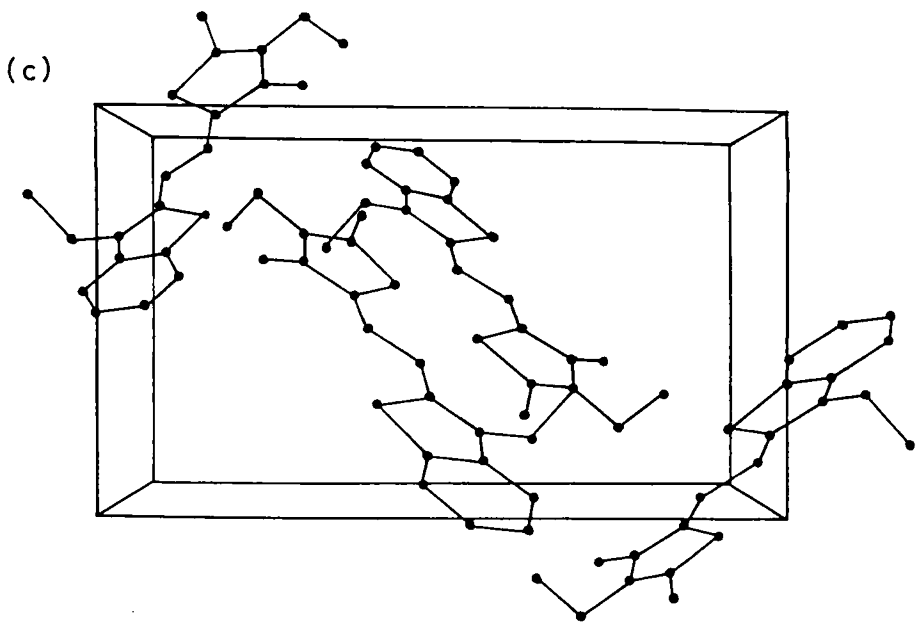


FIGURE 6 (Continued).

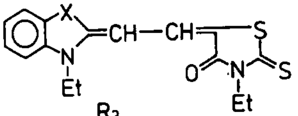
Pope apparatus, and the gas ionization potential Ig was found to be 6.69 eV by UPS,[42] giving a polarization energy of the crystal 1.44 eV.

The α-crystal showed a conductivity of $2.3 \cdot 10^{-10}$ S/cm along *a*-axis, $1.1 \cdot 10^{-11}$ S/cm along *c*-axis and for the β-crystal conductivities found were $3.9 \cdot 10^{-11}$ S/cm along *b*-axis and $7.4 \cdot 10^{-11}$ S/cm along *a*-axis.[34] High anisotropy in conductivity of the α-crystal is consistent with the quasi-one dimensional structure of the crystal. SCLC was observed for the α-crystal at applied fields higher than $4 \cdot 10^2$ V/cm along *a*-axis and $2.5 \cdot 10^3$ V/cm along *c*-axis.

Evaporated film of BTER by rapid evaporation, 150–340 nm/s, at 4.0 Pa vacuum onto SnO_2 coated glass substrate was a red amorphous transparent film which turned to opaque polycrystalline film of α-form in 20 min to 4 h depending on temperature around room temperature.[43,44] The amorphous film showed little photoconductivity while the growth of photo-conductivity was very pronounced during crystallization.[43] A SnO_2/BTER/Cu sandwich cell showed a photo- to dark conductivity ratio of 10^2 at 10^3–2 10^5 V/cm under an irradiance of 13 mW/cm^{-2}, the dark conductivity being 10^{-11}–10^{-12} S/cm. The photo-current reached $7 \cdot 10^{-2}$ A/cm^2 at 100 V applied voltage ($2 \cdot 10^5$ V/cm). However the decay of photo-current after turning off the illumination was very slow, in matter of several hours, presumably due to tremendous amount of traps present in the film.

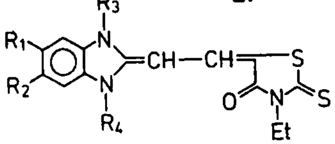
Various structure modifications of merocyanine dyes of the following strucures[45–48] with absorption peaks of the evaporated films covering the whole visible spectrum of λ = 400–650 nm were studied for photo-voltaic properties using the sandwich configuration semitransparent Al, Al_2O_x/dye/Ag.

I

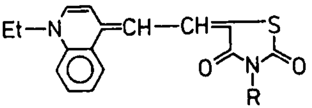


X = S, O

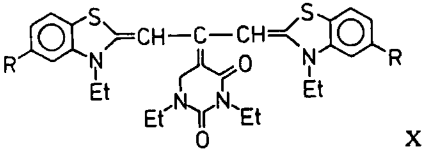
II



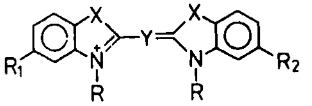
III



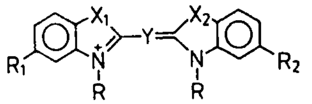
IV



V

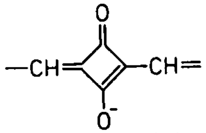


VI

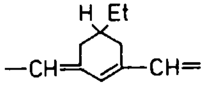


X = $-\text{CMe}_2-$, $-\text{S}-$, $-\text{Se}-$

Y=



(A)



(B)

X_1, X_2 = $-\text{CMe}_2-$, $-\text{S}-$, $-\text{CH}=$

Among them the better ones found are listed in Table II.

POLYVINYLCARBAZOLE TYPE ELECTROPHOTOGRAPHIC MATERIALS

Polyvinylcarbazole-2,4,7-trinitrofluorenone (PVCz-TNF) charge transfer complex shows an absorption band in the visible region. It can be used as a photo-receptor for electrophotography. The dark conductivity of the sandwich configuration SnO_2/

TABLE II

Photovoltaic properties of the sandwich cell Al,Al_2O_x/dye/Ag

Dye	j_{sc}	V_{oc}	Conversion efficiency[a] %
VI, R=Et, R_1=MeO R_2=H, X=S, Y=(B)	40	0.95	1.12
VI, R=Me, R_1=R_2=H X_1=X_2=CMe_2 Y=(A)	28	0.94	0.80
VI, R=Et, R_1=R_2=H, X_1=S, X_2=CMe_2 Y=(A)	20	1.00	0.61

[a] Under 7 mw/cm^2 irradiance.

PVCz-TNF(1:0.5)/Cu showed ohmic behavior at low applied fields and then conformed to a square dependence in its *j*-V characteristics.[49] This was found to be independent of the top electrode used (Cu, Ag or Au). Mobility measurements by time of flight method showed that the hole transport was dispersive satisfying Scher-Montroll relation to give a mobility $\mu_h = 4.1 \cdot 10^{-8}$ cm^2 v^{-1} s^{-1} at $E < 1.8 \cdot 10^5$ at 40°C,[50] and became non-dispersive above 45°C.[51] At high fields the hole mobility increased with $E^{1/2}$ as shown in Figure 7. The electron transport was non-dispersive at 40°C with mobility values much higher than the hole mobility and increased with $E^{1/2}$ at the lowest field used in measurement ($1 \cdot 10^5$/cm). Thus it is clear that the non-ohmic behavior is a bulk effect of the Pool-Frenkel mechanism. The photoconduction action spectrum showed a peak in the visible region at λ590 nm[52] in accord with the charge transfer absorption.

As an electrophotographic photo-receptor a coating of PVCz-TNF was applied to a polyester film base with an evaporated Al surface coating. The film surface

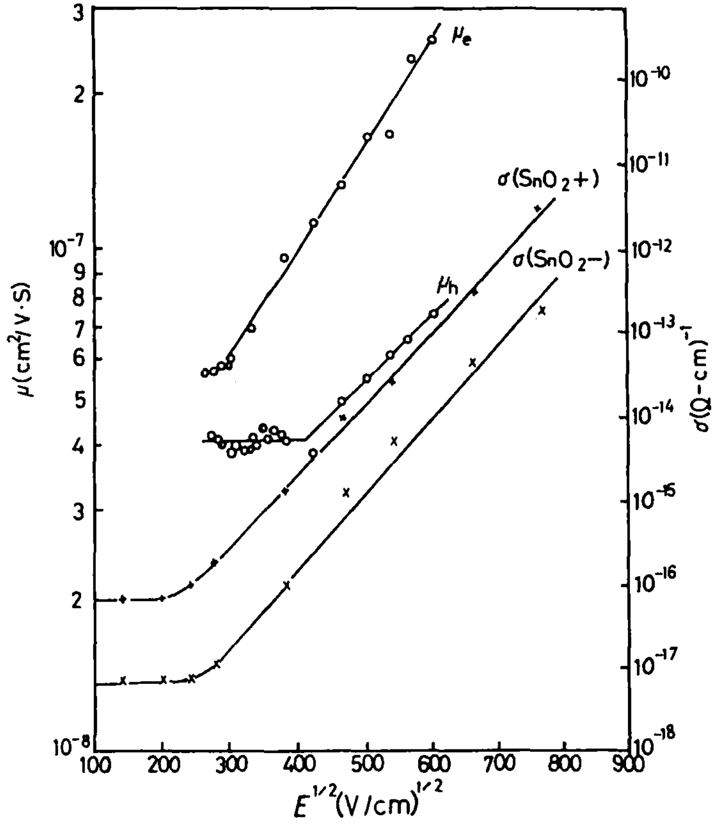


FIGURE 7 Field dependence of the conductivity and hole and electron mobilities of PVK-TNF (1:0.5) at 40°C, thickness 6.1 μm, electrode area 19.6 mm^2.

TABLE III

Nitrofluorenones and CT complex formation with *N*-vinylcarbazole (VCz)

	Electron affinity, eV	Relative degree of conjugation	VCz-NF CT-complex equilibrium constant	Degree of CT
2-nitro	0.43	0.48	0.4	0.50
2,7-di-nitro	0.69	0.52	1.6	0.55
2,4,7-tri-nitro	0.94[a]	1.04	2.4	0.62
2,4,5,7-tetra-nitro	1.21	0.14	2.5	0.67

[a] As reference.

was plasma charged negatively to a high voltage of 400–600 V and the decay of the surface potential was followed under illumination. The kinetics of charging up was found to follow the relation[53]

$$V = V_\infty \exp(-k/t^{1/2})$$

where V_∞ and K are constants with V_∞ found to be proportional to the thickness of the photo-conducting layer. The initial rate of charging decreased with increasing molar ratio PVCz:TNF up to 1:1. The half decay time of the surface potential under illumination for a 6 μm thick layer of PVCz:TNF(1:1) followed the reciprocity law so that $I \cdot t_{1/2}$ being independent of the illumination intensity I when $I < 10$ lux.[54] $I \cdot t_{1/2}$ is usually taken as a measure of the sensitivity of the photo-receptor, a smaller value indicating better sensitivity. $I \cdot t_{1/2}$ values for PVCz-TNF photo-receptor were found to be 6–15. Unpolymerized monomer remaining in PVCz greater than 2% decreased the sensitivity of the photo-receptor and caused pronounced O_3 deterioration.[55]

As PVCz absorbs only in the ultra-violet a large number of dye sensitizers have been synthesized in an attempt to replace TNF for CT complex formation. These dyes include pyrylium salts, benzopyrylium salts, thiopyrylium salts, 3-H indolium salts and 10-H pyrido-indolium salts.[59–61] A two layer photo-receptor consisted of a dye layer on top of poly(vinyl-3-Br-carbazole) showed good electrophotographic sensitivity of 3 lux-s. The dye was a reaction product of 2-(*p*-methoxystyryl)-3-phenyl benzopyrylium perchlorate and 2-(*p*-methoxystyryl)-3-phenyl benzopyran which has absorption peaks at λ570 and λ650 nm.[62]

The degree of charge transfer between mono-, di-, tri- and tetra-nitro-substituted fluorenones and *N*-vinylcarbazole was studied by N_{1s} XPS using *N*-ethyl carbazolium picrate as complete charge transfer.[56] For these nitrofluorenones the electron affinity, CT complex equilibrium constant with *N*-vinylcarbazole as estimated from the relative abundance of the molecular ion peak of mass number 315 to the sum of all peaks from the molecular fragments of mass numbers greater than 42 from mass spectrometry[58] are listed in Table III.

QUANTUM CHEMICAL STUDIES

During the studies of pyrolyzed PAN as organic semiconductor quantum chemical calculations by HMO approximation were carried out for infinite conjugated systems of —C═N—, —C═C—, polyphenylene, polyphenylacetylene, polyphenylenevinylene and polyacene types.[63] In more recent studies graph theory method was applied to the solution of the characteristic equation.[64–68] For conjugated polyenes a semiempirical quantitative relation was presented by Jiang[69] for the electronic absorption frequency of a homologous series of conjugation length n

$$\bar{\nu} = a + b(1/2)^{2/n}$$

where a and b are constants. This equation has been found to fit to experimental data very closely and to have wide applications. A quantum chemical theory gave the HOMO energy levels

$$E = a + b \sin[\pi/(2n + 1)]$$

for the above mentioned homologous series.[70]

Quantum chemical calculations of the electronic energy bands of molecular crystals have been carried out using linear combination atomic orbital–crystal orbital (LCAO-CO) Bloch eigenfunction by variational and perturbation methods.[71–74] The energy of MO in crystal is lower than that in the isolated molecule and widened to a band of certain width depending on the inter-molecular interaction.

Electronic energy band calculations were also extended to charge transfer complexes including *N*-vinylcarbazole-nitrifluorenones,[75] benzene-tetracyanoethylene,[76] pyridine-BX_3 (X═Cl, Br, I) for n,v[77] and π,π[78] complexes and porphin dimer,[79] all using EHMO. It was shown that in the porphin dimer the charge distribution in the porphin molecule showed charge localization to form donor and acceptor centers in the same molecule which contributed to the CT interaction between the porphin molecules in the dimer.

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References

1. Martin Pope and Renyuan Qian, "Electronic Processes in Organic Crystals" (in Chinese), Shanghai Science & Technology Press, 1987.
2. Bingzheng Jiang and Baogong Qian, "Proceedings of National Polymer Conference on Physical Chemistry and Physics of Polymers, Academia Sinica, Changchun, 1961," Science Press, Beijing, 1963, p. 233.
3. Mingdao Tang, *ibid.*, p. 200; *Acta Phys. Sinica*, **19**, 830 (1963).
4. Xuezhou Wu and Jinchang Zhu, *zulun lin*, *ibid.*, p. 208.

5. Rengyuan Li and Baogong Qian, *ibid.*, p. 213.
6. Bingzheng Jiang and Baogong Qian, *ibid.*, p. 226.
7. Shikun Yang, Yunxiang Deng, Haihua Wang, Zhengyao Pan, Lanxin Ye, Shangcai Wu and Shangan Lin, *ibid.*, p. 269.
8. Wenxiang Yang and Baogong Qian, *ibid.*, p. 241.
9. Tai Zhang and Shouxi Chen, *ibid.*, p. 278.
10. Wenxiang Yang and Baogang Qian, *ibid.*, p. 250.
11. Shengqing Lu, Likang Zhang and Mingdao Tang, *Gaofenzi Tongxun*, 330 (1964).
12. Daxun Lu and Wei Hong, *Proc.* (Reference 2) p. 255.
13. Dexi Wang, Dayuan Cui, Boliang Luo, Xiugang Wang and Renjie Wu, *Gaofenzi Tongxun*, 1 (1984).
14. Xianmou Zong and Shuwen Yu, *Proc.* (Reference 2) p. 286.
15. Zhifen Li, Shufan Zhang, Tongming Liu and Xizhe Pan, *Gaofenzi Tongxun*, 162 (1980).
16. Zhifen Li, Zhen Liu and Mingdao Tang, *Kexue Tongbao*, (4), 51 (1963).
17. Yochen Ling, Shufan Zhang, Hansan Shou and Mingdao Tang, *Kexue Tongbao*, (4), 53 (1963).
18. Yuocheng Liu, Xianchi Wu, Chenyi Zhao, Wei Chen, Anchen Yao and Huixiu Gao, *Gaofenzi Tongxun*, 71 (1964).
19. Yoncheng Liu, Xuanchi Wu, Jincang Zhang and Zhongxiao Shi, *Gaofenzi Tongxun*, 477 (1964).
20. Yoncheng Liu, Xuanchi Wu and Zhiqin Jiang, *Gaofenzi Tongxun*, 481 (1964).
21. Yaozeng Huang, Jianqiang Zhou and Jisen Li, *Gaofenzi Tongxun*, 229 (1985).
22. Dianxun Wang, Zurong Shi, Zhongfu Cai and Renyuan Qian *Huaxue Tongbao*, 655 (1980).
23. Zurong Shi and Renyuan Qian, *ibid.*, 42 (1983).
24. Zurong Shi, Zhongfu Cai and Renyuan Qian, *ibid.*, 88 (1982).
25. Shangxian Chen, Kazuhiko Seki, Hiroo Inokuchi, Zurong Shi and Renyuan Qian, *Bull. Chem. Soc. Jpn.*, **56**, 2565 (1983).
26. Anon. (Renyuan Qian, Tongming Liu, Shenqing Lu and Zhongfu Cai) *Acta Chim. Sinica*, **34**, 261 (1976).
27. Zurong Shi and Zhongfu Cai, *Kexue Tongbao*, 792 (1983).
28. Renyuan Qian, Zurong Shi and Zhongfu Cai, *Kexue Tongbao*, (Engl. Ed.), **26**, 522 (1981).
29. Zurong Shi, Qiyun Yang and Longcun Chang, *Kexue Tongbao*, (Engl. Ed.), **31**, 1108 (1986).
30. Zurong Shi and Renyuan Qian, Submitted to *Kexue Tongbao*.
31. Zurong Shi, Jingwen Zhang, Zhongfu Cai, Wenqiu Huang and Renyuan Qian, *J. Appl. Sci. (China)*, **5**, 358 (1987).
32. Renyuan Qian, Shuqin Zhou, Xiangfeng Jin, Zengqi Wang and Shouren Jiang, *J. Appl. Sci. (China)*, **5**, 37 (1987).
33. Xiangfeng Jin, Shuqin Zhou and Renyuan Qian, Preprints, Japan Hardcopy '88, Tokyo, 1988, The Society of Electrophotography of Japan.
34. Renyuan Qian, Xiangfeng Jin and Shuqin Zhou, *Acta Phys. Sinica*, **29**, 992 (1980).
35. Tongming Liu, *Photogr. Sci. Photochem. (China)*, 42 (1986).
36. Hongjun Pan, Songyu Huang and Changshou Zhou, *J. East China Inst. Chem. Technology*, **12**, 583 (1986).
37. Fulin Wang, Jiazuan Ni, Yunfen Xie and Tongming Liu, *J. Inorg. Chem. (China)*, **3**, 35 (1987).
38. Youming Chang, Shengqing Lu and Renyuan Qian, *Phys. Stat. Sol. (a)*, **98**, 37 (1986).
39. Chunli Bai, Youming Chang and Xiaojie Xu, *Kexue Tongbao*, (Engl. Ed.), **28**, 1060 (1983).
40. Fang Guo, Heng Fu, Youming Chang and Shengqing Lu, to be published.
41. Xiangfeng Jin, Marek Zielinski and Martin Pope, *Chemical Phys. Lett.*, **119**, 173 (1985).
42. Dianxun Wang, private communication.
43. Shengqing Lu, Zhongfu Cai, Youming Chang, Xiangfeng Jin, Shuqin Zhou and Renyuan Qian, *Acta Chim. Sinica*, **40**, 657 (1982).
44. Shengqing Lu, Fulin Wang, Benming Chen, Tongming Liu and Xiaodong Deng, *Kexue Tongbao*, 1308 (1987).
45. Songyu Huang, Changshou Zhou, Suying Wang, Singlei Chen and Yushi Pao, *J. East China Inst. Chem. Technology*, 221 (1984).
46. Songyu Huang, Qijun Yin, Suying Wang, Zuguang Yao and Yushi Pao, *Acta Energ. Sol. Sinica*, **6**, 444 (1985).
47. Songyu Huang, Qijun Yin, Rulin Fan and Zhanghua Zhu, *J. East China Inst. Chem. Techn.*, **12**, 745 (1986).
48. He Tian, Songyu Huang and Changshou Zhou, *Acta Phys. Chim. Sinica*, **4**, 314 (1988).
49. Shhangxian Chen, Meixiang Wan, Xinfang Ying and Renyuan Qian, *Kexue Tongbao*, (Engl. Ed.), **26**, 35 (1981).
50. Dalin Yang, Meixiang Wan, Jingwen Zhang, and Renyuan Qian, *Acta Phys. Sinica*, **31**, 1684 (1982).

51. Renyuan Qian, Dalin Yang, Meixiang Wan and Jinwen Zhang, Abstr. China–Japan Joint Symposium on Conduction & Photoconduction in Organic Solids and Related Phenomena, Beijing 1983, p. 73.
52. Tongming Liu, Meixiang Wan, Dalin Yang and Renyuan Qian, *Gaofenzi Tongxun*, 317 (1982).
53. Dewen Chen, Yu Xu and Zhahua Liang, *Polym. Commun.* (*China*), 258 (1985).
54. Dewen Chen, Ping Wu, Shenhua Liang and Fu Yin (Photocopying), **4**, 10 (1986).
55. Yu Xu, Zhenhua Liang and Dewen Chen, *Ganguang Cailiao, (Photosensitive Materials)*, **1**, 20 (1984).
56. Dianxun Wang, Jiabai Qiu, Ruisong Ding and Jinhua Du, *Acta Chim. Sinica*, **42**, 718 (1984).
57. Jiabai Qiu, Ruisong Ding and Jinhuan Du, *Huaxue Tongbao*, 723 (1981).
58. Zeliang Bian, Conghui Wang, Guangzhi Xu, Ruisong Ding and Jiabai Qiu, *Huaxue Tongbao*, (3), 16 (1985).
59. Zhijie Liu, CN Pat. applied 1985.
60. Zhijie Liu, Yong Gong, Shouhu Chen and Jujiu Cao, Abstr. 2nd China–Japan Joint Symposium on Conduction & Photoconduction in Organic Solids and Related Phenomena, Okazaki, Nov. 1986.
61. Zhoongjie Li, Zongren Zhang and Jiuru Guo, *Huaxue Tongbao*, (8), 13 (1985).
62. Zhijie Liu, Yongsheng Lei, Chunho Sun and Jujiu Cao, *Photogr. Sci. Photochem.* (*China*), 1 (1985).
63. Bailin Hao, Desen Lin and Shigang Chen, *Acta Phys. Sinica*, **17**, 289 (1961).
64. Aoqing Tang and Yuansen Jiang, *Zhongguo Kexue*, 218 (1977).
65. Fuji Zhang, *Zhongguo Kexue*, 153 (1979).
66. Zuoxin Wang and Jimin Yan, *Beijing Huagong Xueyuan Xuebao*, (4), 1 (1979).
67. Jimin Yan, *Rev. Quant. Chem.*, **13**, 211 (1981).
68. Zuoxin Wang and Jimin Yan, *Fenzi Kexue Yu Huaxue Yanjiu*, (*Molecule Science & Chemical Research*), 337 (1984).
69. Mingqian Jiang, "Rules of Homologous Linearity of Organic Compounds" (in Chinese), Science Press, Beijing, 1980, p. 364.
70. Guangxian Xu and Yuemin Li, *Zhongguo Kexue*, 136 (1980).
71. Jimin Yan and Qiyuan Zhang, *Kexue Tongbao*, (Engl. Ed.), **28**, 475 (1983).
72. Jimin Yan and Jianguo Zhao, *J. Mol. Sci.* (*China*), **2**, 85 (1984).
73. Jimin Yan, *J. Mol. Sci.* (*China*), **2**, 99 (1984).
74. Jimin Yan and Puwen Zhang, *Kexue Tongbao*, (Engl. Ed.), **31**, 1179 (1986).
75. Jimin Yan and Qiyuan Zhang, *Acta Chim. Sinica*, **42**, 495 (1984).
76. Jimin Yan and Jinkun Liu, *Acta Chim. Sinica*, **42**, 639 (1984).
77. Jimin Yan and Jianguo Zhao, *Kexue Tongbao*, (Engl. Ed.), **30**, 475 (1985).
78. Jimin Yan and Jianguo Zhao, *Int. J. Quant. Chem.*, **27**, 465 (1985).
79. Jimin Yan and Jianguo Zhao, *Acta Physochim. Sinica*, **2**, 541 (1986).